THEORY OF DOUBLET SPECTRA UNDER MAGNETIC PERTURBATION

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ABSTRACT. The problem of a spinning electron moving round the nucleus in the presence of an external magnetic field has been considered from the wave-statistical point of view. The general expressions for energies and wave functions in any field strength have been obtained. The problems of no field, weak field (Zeeman effect) and strong field (Paschen-Back effect) are considered as special cases. The results for the no field case are identical with those obtained in the earlier paper (Kar and Sengupta, 1949). Other results also agree with the well-known spectroscopic formulæ.

In a recent paper the energies and intensities of doublet spectra have been calculated by Kar and Sengupta (1949) by the usual wave-statistical method without splitting the second order wave equation into two linear equations as has been done by Dirac. In the above paper the effect of the external magnetic field has not been considered. Further, although a spin function with half harmonic value is introduced, no generalised wave equation for the spin and revolving motion of the electron is given. Moreover, in that paper the idea of vector coupling between L and S and the formation of the coupled states defined by J and M has been used.

In the present paper we shall dispense with the above idea and shall give a general treatment of the problem taking into account the effect of external magnetic field. We shall at first calculate the energy values and wave functions of a spinning electron moving round a nucleus and under the influence of an external magnetic field. The problems of (*a*) no field (*b*) weak field and (*c*) strong field will then be considered as special cases.

Before we actually go into the problem it may be useful to give a short summary of the previous works on the subject. As early as 1926 Heisenberg and Jordon (1926) first discussed the problem using matrix mechanics. Later on Condon and Shortley (1935) arrived at the same result by a somewhat similar method. Again on starting from Dirac's equations for hydrogenic atom, Darwin (1928) and subsequently Bose and Bose (1944) using Sonine's polynomials, obtained the same general expression for the energy of the spinning electron in any field strength.

The complete wave function for the spinning electron moving round the nucleus is given by (vide Kar and Sengupta *loc. cit.*).

$$\chi_{nlm_l m_s} = \chi_{nlm_l} . \chi'_{m_s}$$

where χ_{nlm_l} and χ'_{m_s} are the orbital and spin wave functions. If we assume the spinning electron to be equivalent to a rotator of mass m_0 and radius a, where a is the radius of gyration of the electron about its centre, then the wave equation satisfied by χ'_{m_s} is the same as that of a rotator. It can be easily shown that the complete function $\chi_{nlm_lm_s}$ satisfies the wave equation,

$$\Delta\chi_{nlm_lm_s} + \frac{8\pi^2 m_0}{h^2}(E_{nls} - V)\,\chi_{nlm_lm_s} = 0 \qquad \ldots \quad (1.1)$$

$$\text{where}\quad \Delta = \left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

$$+\frac{1}{a^2}\left(\frac{1}{\sin\theta'}\frac{\partial}{\partial\theta'}\sin\theta'\frac{\partial}{\partial\theta'} + \frac{1}{\sin^2\theta'}\frac{\partial^2}{\partial\phi'^2}\right) \qquad \ldots \quad (1.2)$$

and

$$E_{nls} = E_{nl} + E_s \qquad \ldots \quad (1.3)$$

E_{nl} being the well known relativistic orbital energy and E_s the spin energy obtained by solving the wave equation for χ'_{m_s}. Thus for the spinning electron moving round the nucleus we get the wave equation, wave functions and energy values respectively from (1.1), (1) and (1.3).

It is evident that the wave function $\chi_{nlm_lm_s}$ is $2(2l+1)$-fold degenerate with respect to m_l and m_s. Now, since any linear combination of these is also a solution of the wave equation, we write for the general wave function

$$\chi_{nl} = \sum_{m_l=-l}^{+l}\ \sum_{m_s=-\frac{1}{2}}^{+\frac{1}{2}} \alpha_{m_lm_s}\chi_{nlm_lm_s} \qquad \ldots \quad (2)$$

where $\alpha_{m_lm_s}$'s are arbitrary constants. It is easily seen that χ_{nl} satisfies the same wave equation as $\chi_{nlm_lm_s}$ viz., equation (1.1).

We shall now consider the effect of the spin-orbit and magnetic perturbations on this system. The spin-orbit perturbation is given by (Thomas (1926))

$$E_{s-0} = \frac{Ze^2}{2m_0^2c^2}\cdot\frac{(LS)}{r^3} \qquad \ldots \quad (3)$$

where L and S represents the orbital and spin angular momentum vectors of the electron. Other symbols have their usual meaning. Now,

$$(LS) = L_xS_x + L_yS_y + L_zS_z$$

$$= \tfrac{1}{2}\{(L_x+iL_y)(S_x-iS_y) + (L_x-iL_y)(S_x+iS_y) + 2L_zS_z\} = -\frac{h^2}{8\pi^2}.\ \text{operator} \qquad \ldots \quad (3.1)$$

$$\text{where,}\quad \text{operator} = e^{i(\phi-\phi')}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)\left(\frac{\partial}{\partial\theta'} - i\cot\theta'\frac{\partial}{\partial\phi'}\right) +$$

$$e^{-i(\phi-\phi')}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}\right)\left(\frac{\partial}{\partial\theta'} + i\cot\theta'\frac{\partial}{\partial\phi'}\right) + 2\frac{\partial^2}{\partial\phi\partial\phi'} \qquad \ldots \quad (3.2)$$

which is obtained by introducing the well known operators associated with $L_x + iL_y$ etc.

Thus the spin-orbit interaction energy becomes,

$$E_{s-0} = -\frac{Ze^2}{m_0^2c^2}\cdot\frac{h^2}{16\pi^2 r^3}\cdot \text{operator} \qquad \dots \quad (4)$$

Now the orbital magnetic moment of the electron is

$$M_l = \frac{e}{2m_0c}L$$

and the spin magnetic moment

$$M_s = \frac{e}{m_0c}S$$

Hence the total magnetic interaction energy in an external magnetic field H along the $z\rightarrow$ axis, is given by

$$E_H = \frac{e}{2m_0c}(LH + 2SH)$$

$$= a(m_l + 2m_s) \qquad \dots \quad (5)$$

where

$$a = -\frac{ehH}{4\pi m_0c} \qquad \dots \quad (5.1)$$

Thus the total perturbation energy is

$$E_{s-0} + E_H = -\frac{Ze^2}{m_0^2c^2}\cdot\frac{h^2}{16\pi^2 r^3} \text{ operator } + a(m_l + 2m_s) \quad \dots \quad (6)$$

We shall now apply the general method of perturbation for degenerate systems to find the change in energy and wave function. Let the changed energy and wave function be,

$$\left.\begin{aligned} E &= E_{nls} + \varepsilon \\ \chi &= \chi_{nl} + \psi \end{aligned}\right\} \qquad \dots \quad (7)$$

where ε and ψ represent small changes in energy and wave function. The wave equation for the perturbed state is given by (Kar and Sengupta *loc. cit.*)

$$\Delta\chi + \frac{8\pi^2 m_0}{h^2}\{E - (V + E_{s-0} + E_H)\}\chi = 0 \qquad (8)$$

On substituting from (7) in (8) and remembering the relation (1.1), we get neglecting second order terms,

$$\Delta\psi + \frac{8\pi^2 m_0}{h^2}(E_{nls} - V)\psi = \frac{8\pi^2 m_0}{h^2}(E_{s-0} + E_H - \varepsilon)\chi_{nl} \qquad (8.1)$$

If we express ψ as a function of the unperturbed wave functions χ_{nl}'s then

$$\psi = \sum_{n'}\sum_{l'} A_{n'l'}\chi_{n'l'} \qquad \dots \quad (8.2)$$

where $A_{n'l'}$'s are small constants. On substituting (8.2) in (8.1) we get

$$\sum_{n'}\sum_{l'}(E_{nls} - E_{n'l's})A_{n'l'}\chi_{n'l'} = (E_{s-0} + E_H - \varepsilon)\chi_{nl} \qquad \dots \quad (9)$$

It is evident that if we multiply both sides of (9) by any of the $2(2l+1)$ functions $\chi_{nlm_l m_s}$ and integrate throughout the five dimensional q-space then the left hand side will vanish due to the orthogonality of the wave functions $\chi_{nlm_l m_s}$. Therefore we get $2(2l+1)$ equations of the type

$$\int (E_{s-0} + E_H - \epsilon)\chi_{nl}\chi_{nlm_l m_s}\, d\tau = 0$$

Or from (2)

$$\sum_{m'_l}\sum_{m'_s} \alpha_{m'_l m'_s} \int (E_{s-0} + E_H - \epsilon)\, \chi_{nlm'_l m'_s}\, \chi_{nlm_l m_s}\, d\tau = 0 \quad \ldots \quad (10)$$

Now it may be easily shown that the well known relations between the associated Legendre functions

$$e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)P_l^{m_l}\, e^{im_l\phi} = -\sqrt{(l-m_l)(l+m_l+1)}\; P_l^{m_l+1}\, e^{i(m_l+1)\phi}$$

$$e^{-i\phi}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}\right)P_l^{m_l}\, e^{im_l\phi} = \sqrt{(l+m_l)(l-m_l+1)}\,P_l^{m_l-1}\, e^{i(m_l-1)\phi}$$

are also valid for $P_s^{m_s}$ with $s=\frac{1}{2}$ and $m_s = \pm\frac{1}{2}$. On using the above relations we get,

$$E_{s-0}\chi_{nlm_l m_s} = -\frac{Ze^2}{m_0^2c^2}\frac{h^2}{16\pi^2 r^3}\Big\{\sqrt{(l+m_l)(l-m_l+1)}\chi_{nlm_l-1,m_s+1}$$
$$+\sqrt{(l-m_l)(l+m_l+1)}\chi_{nlm_l+1,m_s-1} + 2m_l m_s\chi_{nlm_l m_s}\Big\} \quad \ldots \quad (11)$$

On integrating (10) with the help of (11) we can write out the $2(2l+1)$ equations for different values of m_l and m_s. For $m_s=\frac{1}{2}$ we get $(2l+1)$ equations of the type,

$$\alpha_{m_l\frac{1}{2}}\left\{\frac{b}{2}m_l + a(m_l+1) - \epsilon\right\} + \alpha_{m_l+1,-\frac{1}{2}}\frac{b}{2}\sqrt{(l-m_l)(l+m_l+1)} = 0 \quad \ldots \quad (12)$$

and for $m_s = -\frac{1}{2}$ we get $(2l+1)$ equations of the type,

$$\alpha_{m_l,-\frac{1}{2}}\left\{-\frac{b}{2}m_l + a(m_l-1) - \epsilon\right\} + \alpha_{m_l-1,\frac{1}{2}}\frac{b}{2}\sqrt{(l+m_l)(l-m_l+1)} = 0 \quad (12.1)$$

where

$$l \geq m_l \geq -l$$

and

$$b = \frac{Ze^2}{m_0^2c^2}\cdot\frac{h^2}{8\pi^2}\int_0^\infty \frac{R^2(nl)}{r^3}\cdot r^2 dr = \frac{Rhc\alpha^2 z^4}{n^3 l(l+1)(l+\frac{1}{2})} \quad \ldots \quad (12.2)$$

Perturbation energy.—

The $2(2l+1)$ equations given by (12) and (12.1) contain $2(2l+1)$ constants. By eliminating them and solving for ϵ we get in general $2(2l+1)$

roots of ε. We shall now find out these roots. We take the lth equation of (12) obtained by putting $m_l = l$,

$$\alpha_{l,\frac{1}{2}}\{\tfrac{1}{2}bl + a(l+1) - \varepsilon\} = 0 \tag{13}$$

and $-l$th equation of (12.1)

$$\alpha_{-l,-\frac{1}{2}}\{\tfrac{1}{2}bl - a(l+1) - \varepsilon\} = 0 \tag{13.1}$$

From these we get the two roots,

$$\left.\begin{aligned} \varepsilon &= \quad a(l+1) + \tfrac{1}{2}bl \\ \varepsilon &= -a(l+1) + \tfrac{1}{2}bl \end{aligned}\right\} \tag{14}$$

To get the other $4l$ roots we take the m_{l+1}th equation of (12.1),

$$\alpha m_{l,\frac{1}{2}} \cdot \tfrac{1}{2}b\sqrt{(l-m_l)(l+m_l+1)} + \alpha m_l{+}1,{-}\tfrac{1}{2}\{-\tfrac{1}{2}b(m_l+1) + am_l - \varepsilon\} = 0 \ldots \tag{15}$$

If we eliminate $\alpha m_{l\frac{1}{2}}$ and $\alpha m_l + 1, -\frac{1}{2}$ from (15) and (12), we get solving for ε,

$$\varepsilon = a(m_l + \tfrac{1}{2}) - \frac{b}{4} \pm \frac{1}{4}\sqrt{b^2(2l+1)^2 + 4a^2 + 8ab(m_l+\tfrac{1}{2})} \qquad \ldots \tag{15.1}$$

Thus here we get two energy values for each value of m_l. Since m_l here can take up $2l$ values from $l-1$ to $-l$ corresponding to the $2l$ equations of (12), (the lth equation being already considered) we get in all $4l$ values of ε from (15.1) Again from (14) we get two more values of ε. Thus we have altogether $4l+2$ values of ε.

These $4l+2$ values of ε however can be arranged in two groups. It is seen from (14) and (15.1) that when $a=0$ *i.e.*, in the absence of any magnetic field, all the $4l+2$ different energy levels merge into two, ε_1 and ε_2 where,

$$\left.\begin{aligned} \varepsilon_1 &= \tfrac{1}{2}bl \\ \varepsilon_2 &= -\tfrac{1}{2}b(l+1) \end{aligned}\right\} \qquad \ldots \tag{16}$$

Since both levels given by (14) merge to ε_1, it is easily seen that of the $(4l+2)$ levels $(2l+2)$ merge to ε_1 and the remaining $2l$ to ε_2. Thus we see that in the absence of a field a particular level E_{nls} will break up into two under spin-orbit interaction. Their perturbed energies are given by (16). on application of the field ε_1 splits up into $(2l+2)$ different levels. Two of these are given by (14) and the other $2l$ levels are obtained from (15.1) with the positive sign before the radical. They are,

$$\varepsilon_1^{m_l} = a(m_l+\tfrac{1}{2}) - \frac{b}{4} + \frac{1}{4}\sqrt{b^2(2l+1)^2 + 4a^2 + 8ab(m_l+\tfrac{1}{2})} \qquad \ldots \tag{17}$$

where $\qquad l-1 \geq m_l \geq -l$

It is interesting to note that for $b(2l+1) > 2a$ *i.e.*, for weak field, the energies given by (14) are obtained by putting $m_l = l$ and $-l-1$ respectively in (17). Thus in this case all the $(2l+2)$ energy values are obtained from (17) for $\geq m_l \geq -l-1$, which may be conveniently represented by $\varepsilon_1^l, \varepsilon_1^{l-1} \ldots \varepsilon_1^{-l}, \varepsilon_1^{-l-1}$.

The other level ϵ_2 splits into $2l$ different levels whose energies are obtained from (15.1) with negative sign before the radical, namely,

$$\epsilon_2^{m_l} = a(m_l + \tfrac{1}{2}) - \frac{b}{4} - \frac{1}{4}\sqrt{b^2(2l+1)^2 + 4a^2 + 8ab(m_l + \tfrac{1}{2})} \qquad \dots \quad (17.1)$$

where $\qquad l-1 \geq m_l \geq -l$

Wave function.—

Let us next proceed to find out the wave functions associated with these energy values. We shall throughout neglect ψ, the small correction in the wave function due to perturbation. However, the perturbation also affects the degeneracy of the wave functions and as such modifies the unperturbed wave functions. The modification of this type is often called the zero order correction of the wave function due to perturbation. It may be calculated in the following way.

We have taken the unperturbed wave function in the general form χ_{nl} given in (2), in which $\alpha_{m_l m_s}$'s are arbitrary constants. Thus the problem of finding out the zero-order-corrected wave functions reduces itself to finding the values of $\alpha_{m_l m_s}$'s for different perturbed energy values. To do this we substitute any particular value of ϵ from (17) or (17.1) in the $(4l+2)$ equations of (12) and (12.1). Then we get $(4l+2)$ equations connecting $(4l+2)$ arbitrary constants $\alpha_{m_l m_s}$'s. On combining these equations with the general averaging condition

$$\sum_{m_l} \sum_{m_s} \alpha^2_{m_l m_s} = 1 \qquad \dots \quad (18)$$

we can easily find out the values of these constants.

If we take the energy values given in (17) and substitute them in equations (12) and (12.1), we see that all $\alpha_{m_l m_s}$ except $\alpha_{m_l \frac{1}{2}}$ and $\alpha_{m_l+1, -\frac{1}{2}}$ vanish. For these two we get from (12)

$$\frac{\alpha_{m_l \frac{1}{2}}}{\alpha_{m_l+1, -\frac{1}{2}}} = -\frac{\frac{1}{2}b\sqrt{(l-m_l)(l+m_l+1)}}{\frac{1}{2}bm_l + a(m_l+1) - \epsilon_1^{m_l}} \qquad \dots \quad (19)$$

utilising the relation (18) and after some work we get,

$$\left.\begin{aligned} \alpha^2_{m_l \frac{1}{2}} &= \frac{-\frac{1}{2}b(m_l+1) + am_l - \epsilon_1^{m_l}}{-\frac{1}{2}b + a(2m_l+1) - 2\epsilon_1^{m_l}} \\ \alpha^2_{m_l+1, -\frac{1}{2}} &= \frac{\frac{1}{2}bm_l + a(m_l+1) - \epsilon_1^{m_l}}{-\frac{1}{2}b + a(2m_l+1) - 2\epsilon_1^{m_l}} \end{aligned}\right\} \qquad \dots \quad (19.1)$$

Thus the wave functions associated with the given energy values $\epsilon_1^{m_l}$'s are,

$$\chi_{nl\epsilon_1 m_l} = \alpha_{m_l \frac{1}{2}} \chi_{nlm_l \frac{1}{2}} + \alpha_{m_l+1, -\frac{1}{2}} \chi_{nlm_l+1, -\frac{1}{2}} \qquad \dots \quad (20)$$

where $\qquad l \geq m_l \geq -l-1$

and $\alpha_{m_l\frac{1}{2}}$, $\alpha_{m_l+1,-\frac{1}{2}}$ are given by (19.1). Similarly if we take the energy values given in (17.1) and substitute them in the equations (12) and (12.1) we get as before for the non-vanishing coefficients $\alpha_{m_l\frac{1}{2}}$ and $\alpha_{m_l+1,-\frac{1}{2}}$,

$$\frac{\alpha_{m_l\frac{1}{2}}}{\alpha_{m_l+1,-\frac{1}{2}}}=\frac{-\frac{1}{2}b\sqrt{(l-m_l)(l+m_l+1)}}{\frac{1}{2}bm_l+a(m_l+1)-\epsilon_2^{m_l}} \quad \ldots \quad (21)$$

and

$$\left.\begin{aligned} \alpha^2_{m_l\frac{1}{2}} &= \frac{-\frac{1}{2}b(m_l+1)+am_l-\epsilon_2^{m_l}}{-\frac{1}{2}b+a(2m_l+1)-2\epsilon_2^{m_l}} \\ \alpha^2_{m_l+1,-\frac{1}{2}} &= \frac{\frac{1}{2}bm_l+a(m_l+1)-\epsilon_2^{m_l}}{-\frac{1}{2}b+a(2m_l+1)-2\epsilon_2^{m_l}} \end{aligned}\right\} \quad \ldots \quad (21.1)$$

Thus the wave functions associated with the energy values $\epsilon_2^{m_l}$'s are,

$$\chi_{nl\epsilon_2^{m_l}} = \alpha_{m_l\frac{1}{2}}\chi_{nlm_l\frac{1}{2}}-\alpha_{m_l+1,-\frac{1}{2}}\chi_{nlm_l+1,-\frac{1}{2}} \quad \ldots \quad (22)$$

where
$$l-1 \geq m_l \geq -l$$

and $\alpha_{m_l\frac{1}{2}}$, $\alpha_{m_l+1,-\frac{1}{2}}$ are given by (21.1). Here we have taken $\alpha_{m_l+1,-\frac{1}{2}}$ negative, for it can be easily shown from (17.1) that $\epsilon_2^{m_l} < \frac{1}{2}bm_l+a(m_l+1)$ and so from (21) the ratio $\alpha_{m_l\frac{1}{2}}/\alpha_{m_l+1,-\frac{1}{2}}$ should be negative.

Thus the equations (17), (17.1), (20) and (22) give the general values of the energies and wave functions of the electron in any field strength. From these we can calculate the frequencies and intensities of the lines resulting from any transition. The general expression for the intensity of the line in any field strength is rather complicated. We shall, however, consider a simple case and calculate the intensities of the ten components of sodium D_1 and D_2 lines in any field strength. But before that we shall consider some special cases.

No field case.—

As already pointed out for $H=0$ *i.e.*, $a=0$ the $(2l+2)$ levels of energies $\epsilon_1^{m_l}$'s given in (17) merge into one level ϵ_1 given by (16). Similarly the $2l$ levels given by (17.1) merge into another level ϵ_2. The total energies of these two levels are given by (*vide* equations (7) and (1.3))

$$\left.\begin{aligned} E_1 &= E_{nl}+E_s+\epsilon_1 \\ E_2 &= E_{nl}+E_s+\epsilon_2 \end{aligned}\right\} \quad (23)$$

Scince E_s is constant, it will not affect the calculation of frequencies of different lines. Neglecting it and substituting the values of E_{nl}, ϵ_1 and ϵ_2 it may be easily seen that (23) is identical with the well known spin-relativity formula.

It is evident that ϵ_1 and ϵ_2 levels are now $(2l+2)$- and $(2l)$- fold degenerate. The associated wave functions can be easily found from (20) and (22) by putting $a=0$. Thus the $(2l+2)$ wave functions for ϵ_1 are given by,

$$\chi_{nl\epsilon_1}^{m_l} = \sqrt{\frac{(l+m_l+1)}{2l+1}}\,\chi_{nlm_l\frac{1}{2}} + \sqrt{\frac{(l-m_l)}{2l+1}}\,\chi_{nlm_l+1,\,-\frac{1}{2}} \quad \ldots \quad (24)$$

where $$l \geq m_l \geq -l-1$$

and the $2l$ wave functions for ϵ_2 level are given by

$$\chi_{nl\epsilon_2}^{m_l} = \sqrt{\frac{(l-m_l)}{2l+1}}\,\chi_{nlm_l\frac{1}{2}} - \sqrt{\frac{(l+m_l+1)}{2l+1}}\,\chi_{nlm_l+1,\,-\frac{1}{2}} \quad \ldots \quad (24{\cdot}1)$$

where, $$l-1 \geq m_l \geq -l$$

If we write $m=m_l+m_s$ remembering that m has the value $m_l+\frac{1}{2}$ for both the functions on the right hand side of (24) and (24·1) then it is easily seen that they are identical with the wave functions given in the earlier paper (Kar-Sengupta *loc. cit.*) for the states $j=l+\frac{1}{2}$ and $j=l-\frac{1}{2}$. Thus the different lines and their intensities can now be calculated in the same way as before.

Weak field case (Zeeman effect).—

In this case $b >> a$, since H is small. Hence we neglect a^2 compared to b^2. Thus from (17) we get

$$\epsilon_1^{m_l} = \frac{b}{2}l + ag(m_l+\tfrac{1}{2});\; g=\frac{2l+2}{2l+1} \quad \ldots \quad (25)$$

where $$l \geq m_l \geq -l-1$$

and g is the Lande factor for doublets with $j=l+\frac{1}{2}$. Similarly from (17·1) we get,

$$\epsilon_2^{m_l} = -\frac{b}{2}(l+1) + ag(m_l+\tfrac{1}{2});\; g=\frac{2l}{2l+1} \quad \ldots \quad (25{\cdot}1)$$

where $$l-1 \geq m_l \geq -l$$

and g is the Lande factor for doublets with $j=l-\frac{1}{2}$. If we write $m=m_l+\frac{1}{2}$ then it is easily seen that (25) and (25·1) are identical with Lande's formula for Zeeman separations. For vanishingly small fields, the wave functions associated with (25) and (25·1) are still same as in the no field case and are given by (24) and (24·1) respectively. We shall now calculate the intensities of the Zeeman components of the lines resulting from any transition $nl \rightarrow n'l'$

$(l'=l-1)$. For no field we get in general three lines from the above transition. They are,

$$(1)\quad nl\epsilon_1 \rightarrow n'l'\epsilon'_1$$

$$(2)\quad nl\epsilon_2 \rightarrow n'l'\epsilon'_1$$

$$(3)\quad nl\epsilon_2 \rightarrow n'l'\epsilon'_2$$

The fourth line as was shown in the previous paper will have zero intensity. In a weak magnetic field both ϵ_1, ϵ_2 and ϵ'_1, ϵ'_2 break up into several levels, their energies being given by (25) and (25·1). From any one of these initial levels $\epsilon_1^{m_l}$ or $\epsilon_2^{m_l}$ in general three different transitions may occur. These are characterised by three different values of Δm_l, *viz.*, $\Delta m_l = 0, \pm 1$. For the transitions with $\Delta m_l = 0$, only the Z-component of the electric moment (M_z) exists. Hence the resulting vibrations are along the Z-direction and we get the π-components of the Zeeman pattern. For $\Delta m_l = \pm 1$ we get the σ-components. Since in transverse observation intensities of the lines are proportional to the square of the moments, we shall have to calculate M_x, M_y and M_z for different transitions from the wave functions (24) and (24.1). Calculations are same as in the previous paper (Kar-Sengupta *loc. cit.*) and we shall only give the results here.

(1) For the line $nl\epsilon_1 \rightarrow n'l'\epsilon'_1$

$$\left.\begin{aligned} \Delta m_l = 0 \qquad & M_z^2 = \frac{(l-m_l)(l+m_l+1)}{(2l+1)^2} R^2(nl;\ n'l-1) \\ \Delta m_l = \pm 1 \quad & M_x^2 = M_y^2 = \frac{1}{4}\frac{(l \mp m_l)(l \mp m_l \mp 1)}{(2l+1)^2} R^2(nl;\ n'l-1) \end{aligned}\right\} \quad \dots \quad (26)$$

(2) for the line $nl\epsilon_2 \rightarrow n'l'\epsilon'_1$

$$\left.\begin{aligned} \Delta m_l = 0 \quad & M_z^2 = \frac{(2m_l+1)^2}{(4l^2-1)^2} R^2(nl;\ n'l-1) \\ \Delta m_l = +1, \ & M_x^2 = M_y^2 = \frac{(l-m_l-1)(l+m_l+1)}{(4l^2-1)^2} R^2(nl;\ n'l-1) \\ \Delta m_l = -1, \ & M_x^2 = M_y^2 = \frac{(l+m_l)(l-m_l)}{(4l^2-1)^2} R^2(nl;\ n'l-1) \end{aligned}\right\} \quad \dots \quad (26.1)$$

(3) for the line $nl\epsilon_2 \rightarrow n'l'\epsilon'_2$

$$\left.\begin{aligned} \Delta m_l = 0 \qquad & M_z^2 = \frac{(l+m_l)(l-m_l-1)}{(2l-1)^2} R^2(nl,\ n'l-1) \\ \Delta m_l = +1, \ & M_x^2 = M_y^2 = \frac{1}{4}\frac{(l-m_l-1)(l-m_l-2)}{(2l-1)^2} R^2(nl;\ n'l-1) \\ \Delta m_l = -1, \ & M_x^2 = M_y^2 = \frac{1}{4}\frac{(l+m_l)(l+m_l-1)}{(2l-1)^2} R^2(nl;\ n'l-1) \end{aligned}\right\} \quad \dots \quad (26.2)$$

If we write $m = m_l + \frac{1}{2}$ and $j = l + \frac{1}{2}$ for the initial state ϵ_1 and $j = l - \frac{1}{2}$ for the initial state ϵ_2 then the above formulæ reduce to the well known relations for the intensities of the Zeeman components first derived empirically by Ornstein and Burger (1924).

Strong field case (Paschen-Back effect).

In this case $a >> b$. Hence we get from (17), neglecting b^2 compared with a^2,

$$\epsilon_1^{m_l} = a(m_l + 1) + \tfrac{b}{2} m_l \qquad \ldots \quad (28)$$

where $\quad l - 1 \geq m_l \geq -l$

Similarly from (17.1) we get,

$$\epsilon_2^{m_l} = a m_l - \tfrac{b}{2}(m_l + 1) \qquad \ldots \quad (28.1)$$

where $\quad l - 1 \geq m_l \geq -l$

The remaining two energy values ϵ_1^l and ϵ_1^{-l-1} are given by (14). The wave functions can be easily calculated from (20) and (22). They are,

$$\left.\begin{aligned} &\chi_{nl\epsilon_1^{m_l}} = \chi_{nlm_l \frac{1}{2}} \quad \text{for } l \geq m_l \geq -l \\ \text{and} \quad &\chi_{nl\epsilon_1^{-l-1}} = \chi_{nlm_l = -l, -\frac{1}{2}} \end{aligned}\right\} \qquad \ldots \quad (29)$$

giving the $(2l+2)$ wave functions associated with $(2l+2)$ energy values $\epsilon_1^{m_l}$. Similarly the wave functions associated with $\epsilon_2^{m_l}$'s are given by,

$$\chi_{nl\epsilon_2^{m_l}} = \chi_{nlm_l+1, -\frac{1}{2}} \qquad \ldots \quad (29.1)$$

where $\quad l - 1 \geq m_l \geq -l$

with the above results we can calculate the different lines and their intensities in the Paschen-Back limit. It is easily seen that all the energies given by (28) and (28.1) can be incorporated in the single formula.

$$\epsilon = a(m_l + 2m_s) + b m_l m_s \qquad \ldots \quad (30)$$

where $\quad m_s = \pm\frac{1}{2}$ and $l \geq m_l \geq -l$

and the corresponding wave functions are given by $\chi_{nlm_l m_s}$. Equation (30) gives the most commonly used form for the energy in the Paschen-Back limit. It is easily seen on comparing the energies in the weak (vide (25) and (25.1)) and strong (vide (28) and (28.1)) magnetic fields that in both the cases $\epsilon_1^{m_l} > \epsilon_2^{m_l}$. Evidently this is also true for any intermediate field strength (vide (15.1)). This explains the well known empirical rule that no two levels in the Zeeman and Paschen-Back limits with the same value of m cross each other. If we neglect b compared to a in (30), then for allowed transitions we have,

$$\Delta\epsilon = a\Delta m_l$$

where $\quad \Delta m_l = 0, \pm 1;$

This gives three lines exactly as in Lorentz triplet. Calculations of the intensities for this case also give the same value for the three lines as is to be found in the so called normal triplet, namely, the outer component has half the intensity of the middle one.

Calculation of the intensities of the ten components of sodium D-lines in any field strength.—

The sodium D_1 line results from the transition $3^2P_{\frac{3}{2}} \rightarrow 3^2S_{\frac{1}{2}}$, which breaks up into six components in a magnetic field. The D_2-line results from the transition $3^2P_{\frac{1}{2}} \rightarrow 3^2S_{\frac{1}{2}}$, which breaks up into four components in a magnetic field.

Energies and wave functions for the initial states $3^2P_{\frac{3}{2}}$ and $3^2P_{\frac{1}{2}}$.—

$^2P_{\frac{3}{2}}$ level breaks up into four different levels in a magnetic field H. They are obtained by writing $m_l = 1, 0, -1$ and -2 respectively in (17). Thus,

$$\epsilon_1^1 = 2a + \frac{b}{2}; \quad \epsilon_1^0 = \frac{a}{2} - \frac{b}{4} + \frac{\Delta}{2}; \quad \epsilon_1^{-1} = -\frac{a}{2} - \frac{b}{4} + \frac{\Delta'}{2}; \quad \epsilon_1^{-2} = -2a + \frac{b}{2} \quad \dots \quad (31)$$

where

$$\left.\begin{aligned} \Delta &= \tfrac{1}{2}\sqrt{9b^2 + 4a^2 + 4ab} \\ \Delta' &= \tfrac{1}{2}\sqrt{9b^2 + 4a^2 - 4ab} \end{aligned}\right\} \quad \dots \quad (31.1)$$

The four associated wave functions are given by, (vide (20) and (19 1))

$$\left.\begin{aligned} \chi_{31\epsilon_1^1} &= \chi_{311\frac{1}{2}} \\ \chi_{31\epsilon_1^0} &= A_{0\frac{1}{2}}\,\chi_{310\frac{1}{2}} + A_{1,-\frac{1}{2}}\,\chi_{311,-\frac{1}{2}} \\ \chi_{31\epsilon_1^{-1}} &= A_{-1\frac{1}{2}}\,\chi_{31,-1\frac{1}{2}} + A_{0,-\frac{1}{2}}\,\chi_{310,-\frac{1}{2}} \\ \chi_{31\epsilon_1^{-2}} &= \chi_{31,-1,-\frac{1}{2}} \end{aligned}\right\} \quad \dots \quad (32)$$

where,

$$\left.\begin{aligned} A_{0\frac{1}{2}} &= \sqrt{\frac{1}{2}\left(1 + \frac{a+\frac{b}{2}}{\Delta}\right)}; \quad A_{-1,\frac{1}{2}} = \sqrt{\frac{1}{2}\left(1 + \frac{a-\frac{b}{2}}{\Delta'}\right)} \\ A_{1,-\frac{1}{2}} &= \sqrt{\frac{1}{2}\left(1 - \frac{a+\frac{b}{2}}{\Delta}\right)}; \quad A_{0,-\frac{1}{2}} = \sqrt{\frac{1}{2}\left(1 - \frac{a-\frac{b}{2}}{\Delta'}\right)} \end{aligned}\right\} \quad \dots \quad (32.1)$$

$^2P_{\frac{1}{2}}$ level breaks up into two levels in a magnetic field. They are obtained by writing $m_l = 0, -1$ in (17.1). Thus,

$$\epsilon_2^0 = \frac{a}{2} - \frac{b}{4} - \frac{\Delta}{2}; \quad \epsilon_2^{-1} = -\frac{a}{2} - \frac{b}{4} - \frac{\Delta'}{2} \quad \dots \quad (33)$$

Δ and Δ' being given by (31.1). The associated wave functions obtained from (22) and (21.1) are,

$$\left.\begin{aligned} \chi_{31\epsilon_2^0} &= A_{0\frac{1}{2}}\,\chi_{310\frac{1}{2}} - A_{1,-\frac{1}{2}}\,\chi_{311,-\frac{1}{2}} \\ \chi_{31\epsilon_2^{-1}} &= A_{-1\frac{1}{2}}\,\chi_{31,-1\frac{1}{2}} - A_{0,-\frac{1}{2}}\,\chi_{310,-\frac{1}{2}} \end{aligned}\right\} \quad \dots \quad (34)$$

where,

$$\left.\begin{aligned} A_{0\frac{1}{2}} &= \sqrt{\frac{1}{2}\left(1 - \frac{a+\frac{b}{2}}{\Delta}\right)}; \quad A_{-1,\frac{1}{2}} = \sqrt{\frac{1}{2}\left(1 - \frac{a-\frac{b}{2}}{\Delta'}\right)} \\ A_{1,-\frac{1}{2}} &= \sqrt{\frac{1}{2}\left(1 + \frac{a+\frac{b}{2}}{\Delta}\right)}; \quad A_{0,-\frac{1}{2}} = \sqrt{\frac{1}{2}\left(1 + \frac{a-\frac{b}{2}}{\Delta'}\right)} \end{aligned}\right\} \quad \dots \quad (34.1)$$

Energies and wave functions for the final state $3^2S_{\frac{1}{2}}$.—

Here energies are obtained as before from (17). They are,

$$\epsilon_1^0 = a + b' \,;\; \epsilon_1^{-1} = -a + b' \qquad \ldots \quad (35)$$

b' is the value of bl for $l = 0$ (vide (12.2)). The associated wave functions are given by (vide (20)).

$$\left.\begin{aligned} \chi_{30\epsilon_1^0} &= \chi_{300\frac{1}{2}} \\ \chi_{30\epsilon_1^{-1}} &= \chi_{300,-\frac{1}{2}} \end{aligned}\right\} \qquad \ldots \quad (36)$$

we shall now calculate the intensities of the six lines resulting from the transition $3^2P_{\frac{3}{2}} \rightarrow 3^2S_{\frac{1}{2}}$. We have here

four initial levels ——→ $\epsilon_1^1 \quad \epsilon_1^0 \quad \epsilon_1^{-1} \quad \epsilon_1^{-2}$

two final levels ——→ $\epsilon_1^0 \quad \epsilon_1^{-1}$

Since for allowed transitions we must have $\Delta m_l = 0, \pm 1$ we get altogether six lines as shown by the arrows. The transitions $\epsilon_1^0 \rightarrow \epsilon_1^0$ and $\epsilon_1^{-1} \rightarrow \epsilon_1^{-1}$ give the π-components. Other transitions give rise to the σ-components. The respective moments and hence the intensities can be easily calculated from the wave functions already given. Thus we get for the two π-components,

$$(1) \quad \epsilon_1^0 \rightarrow \epsilon_1^0 \qquad M_z^2 = \frac{R^2(31;30)}{6}\left(1 + \frac{a + \frac{b}{2}}{\Delta}\right)$$

$$(2) \quad \epsilon_1^{-1} \rightarrow \epsilon_1^{-1} \qquad M_z^2 = \frac{R^2(31;30)}{6}\left(1 - \frac{a - \frac{b}{2}}{\Delta'}\right)$$

and for the four σ-components,

$$(3) \quad \epsilon_1^1 \rightarrow \epsilon_1^0 \qquad M_x^2 = M_y^2 = \frac{R^2(31;30)}{6}$$

$$(4) \quad \epsilon_1^0 \rightarrow \epsilon_1^{-1} \qquad M_x^2 = M_y^2 = \frac{R^2(31;30)}{12}\left(1 - \frac{a + \frac{b}{2}}{\Delta}\right)$$

$$(5) \quad \epsilon_1^{-1} \rightarrow \epsilon_1^0 \qquad M_x^2 = M_y^2 = \frac{R^2(31;30)}{12}\left(1 + \frac{a - \frac{b}{2}}{\Delta'}\right)$$

$$(6) \quad \epsilon_1^{-2} \rightarrow \epsilon_1^{-1} \qquad M_x^2 = M_y^2 = \frac{R^2(31;30)}{6} \qquad (37)$$

The intensities of four lines resulting from the transition $3^2P_{\frac{1}{2}} \rightarrow 3^2S_{\frac{1}{2}}$ can be similarly calculated.

Here we have,

two initial levels ——→ $\epsilon_2^0 \quad \epsilon_2^{-1}$

two final levels ——→ $\epsilon_1^0 \quad \epsilon_1^{-1}$

The resulting transitions are shown by arrows. We get for the two π-components,

$$\left.\begin{array}{lll}
(1) & \epsilon_2^0 \rightarrow \epsilon_1^0 & M_z^2 = \dfrac{R^2(31;\,30)}{6}\left(1 - \dfrac{a+\frac{b}{2}}{\Delta}\right) \\[2ex]
(2) & \epsilon_2^{-1} \rightarrow \epsilon_1^{-1} & M_z^2 = \dfrac{R^2(31;\,30)}{6}\left(1 + \dfrac{a-\frac{b}{2}}{\Delta'}\right) \\[2ex]
\multicolumn{3}{l}{\text{and for the two } \sigma\text{-components,}} \\[1ex]
(3) & \epsilon_2^0 \rightarrow \epsilon_1^{-1} & M_x^2 = M_y^2 = \dfrac{R^2(31;\,30)}{12}\left(1 + \dfrac{a+\frac{b}{2}}{\Delta}\right) \\[2ex]
(4) & \epsilon_2^{-1} \rightarrow \epsilon_1^0 & M_x^2 = M_y^2 = \dfrac{R^2(31;\,30)}{12}\left(1 - \dfrac{a-\frac{b}{2}}{\Delta'}\right)
\end{array}\right\} \quad \ldots \quad (38)$$

Since for transverse observation the intensities are proportional to M_z^2 and M_x^2, equations (37) and (38) give the relative intensities of the ten components of sodium D-lines in any field strength. As already pointed out these equations have also been derived by Heisenberg and Jordon (1926) from matrix mechanics.

In conclusion we may note that the whole theory given above is based on the introduction of half-harmonic for representing the spin motion of the electron. There are, however, two difficulties in taking half-harmonic in the spin function. Firstly, it makes the wave function double valued and secondly there is no apparent reason why the electron should have the spin quantum number s always equal to $\frac{1}{2}$ and not other half integral values *viz.*, $\frac{3}{2}$, $\frac{5}{2}$ etc. The first question has already been discussed in the previous paper (Kar-Sengupta *loc. cit.*). The second objection may be removed if we remember the condition of boundedness of the wave functions. It is well known that for physically valid solutions the probability density

$$\rho = X'^2_{m_s} d\tau = (P_s^{m_s})^2 \sin^2\theta' d\theta' d\phi'$$

should be both single valued and bounded *i.e.*, it must have finite values throughout the q-space. The values of the half-harmonic Legendre functions can be obtained by solving the well known wave equation for the rotator by the usual power series method. The two functions with $S = \frac{1}{2}$, are

$$P_{\frac{1}{2}}^{\frac{1}{2}} = \sin^{\frac{1}{2}}\theta' \quad \text{and} \quad P_{\frac{1}{2}}^{-\frac{1}{2}} = \frac{\cos\theta'}{\sin^{\frac{1}{2}}\theta'}$$

It is easily seen that though the second half-harmonic Legendre function is not bounded, the probability density for both the functions are bounded. Thus the above half-harmonic functions with $s = \frac{1}{2}$ give physically valid solutions. However, if we write out the four half-harmonic functions with $s = \frac{3}{2}$ and $m_s = \pm\frac{1}{2}$, $\pm\frac{3}{2}$, then it will be evident that the first three satisfy the condition of boundedness of the density function, but the fourth function with $m_s = -\frac{3}{2}$ does not. Thus with $S = \frac{3}{2}$, the allowed half-harmonic values of m_s are $\pm\frac{1}{2}, +\frac{3}{2}$, while the value $-\frac{3}{2}$ is forbidden. But this non-symmetry in the values of m_s appears to be physically untenable, for there is no fundamental difference between the positive and negative values of m_s. This argument also applies to other higher half-harmonic functions. Thus we may conclude that half-harmonic values of S higher than $\frac{1}{2}$ are really forbidden. They do not give a set of physically valid solutions.

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